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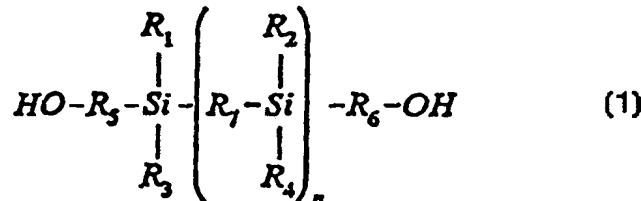
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(54) Title: NON-ELASTOMERIC POLYURETHANE COMPOSITIONS

(57) Abstract

The present invention relates to a non-elastomeric polyurethane composition which includes a chain extender of general formula (1) wherein R₁, R₂, R₃, R₄, R₅, and R₆, are the same or different and selected from an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical; R₇ is a divalent linking group or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical; and n is 0 or greater. The non-elastomeric polyurethane composition has improved mechanical properties, clarity and/or degradation resistance and may be used to produce medical devices, articles or implants.



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NON-ELASTOMERIC POLYURETHANE COMPOSITIONS

The present invention relates to non-elastomeric polyurethane compositions based on silicon-containing chain extenders characterised by high flexural modulus, high glass transition and heat distortion temperatures. These polyurethane compositions are useful for applications requiring high impact resistance, flexural strength, and other structural properties similar to engineering thermoplastics, and in particular for use in above ambient temperature end-use environments.

Polyurethanes represents a broad class of materials formed by reacting chemical compounds bearing functional groups such as isocyanate and hydroxyl. A wide range of polymers with a variety of properties ranging from elastomers to rigid materials can be prepared by selecting a suitable combination of reagents in various proportions. Of these materials, polyurethane elastomers formed by reacting a polyol (typical molecular weight 500 to 4000) with a diisocyanate and a chain extender (low molecular weight diol of molecular weight less than 500), form an important class of commercially useful materials. The methods of synthesis and studies on structure property relationships of these materials are abundant in the polyurethane literature¹.

The polyurethanes formed by reacting only the chain extender and the diisocyanate are generally very rigid with high flexural modulus, and are often difficult to process due to high melting temperatures. For example, a polyurethane prepared from a common diisocyanate 4,4'-methylenediphenyldiisocyanate (MDI) and 1,4-butanediol (BDO) generally melts at temperatures above 210°C which is well above the thermal decomposition temperature of the urethane linkage². Further, such materials are generally very brittle and have poor mechanical properties. Alternatively, harder grades of polyurethane elastomers prepared using a relatively lower proportion of the polyol component usually have a low heat distortion temperatures, primarily due to the presence of the polyol component, usually with a glass transition below ambient temperature.

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Development of polyurethane compositions with high flexural modulus combined with high heat distortion temperatures and thermal processability would provide a new range of rigid materials with strength required for applications in high temperature end-use environments.

5 The hard polyurethane compositions disclosed in US Patent No. 4,101,529 are made by reacting polyisocyanates with mixtures of cycloaliphatic diols and low molecular weight diol chain extenders such as ethylene glycol and low molecular weight active hydrogen containing materials such as trimethylolpropane, and optionally a polymeric polycarbonate diol. These compositions are characterised
10 by heat distortion temperature of at least 88°C (measured by ASTM D-648 at 264 psi) and hardness of at least 75 Shore D. Similarly, US Patent No. 4,808,690 discloses polyurethane compositions with high heat distortion temperatures that are highly cross-linked, and are made by reacting a polyisocyanate prepolymer and a polyhydric alcohol having from 2 to 8 hydroxyl groups in combination with a
15 polyester polyol. Such polyurethanes are expected to be difficult to thermally process due to their highly cross-linked nature.

United States Patent No. 4,822,827 describes thermoplastic polyurethane compositions with high glass transition temperatures based on reacting a polyisocyanate and a particular combination of chain extenders including
20 cycloalkane diol, optionally in the presence of a minor amount of high molecular weight polyol. It is also disclosed that only certain members of the new polymers are optically clear.

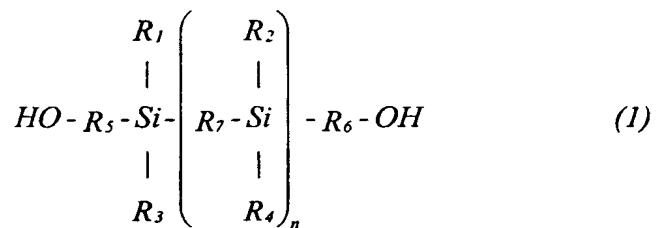
The compositions disclosed in US Patent No. 4,101,529, US Patent No. 4,393,186, US Patent No. 4,808,690 and US Patent No. 4,822,827 all contain a
25 polyol for example polyester, polycarbonate or polyether as part of the polyurethane structure. This would make the prior art compositions susceptible to possible degradation under oxidative and hydrolytic environments, particularly high temperature environments which may limit their applications. Development of new polyurethane compositions which are free of segments derived from
30 polyols while overcoming most of the disadvantages of the prior art compositions,

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would broaden the applications of these materials to areas such as medical devices and implants.

Accordingly, a requirement exists to develop polyurethanes which are easily processable and have a high flexural modulus, high heat distortion 5 temperature, optical clarity, and resistance to degradation.

According to one aspect, the present invention provides a non-elastomeric polyurethane composition which includes a chain extender of the general formula (1)



10 wherein

R_1 , R_2 , R_3 , R_4 , R_5 and R_6 are the same or different and selected from an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical;

15 R_7 is a divalent linking group or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical; and

n is 0 or greater, preferably 2 or less.

The term "non-elastomeric" in the present context refers to polyurethanes having a % elongation of up to about 200%, generally up to about 100%.

20 The term "chain extender" in the present context means any compound having at least two functional groups per molecule capable of reacting with the isocyanate group and generally in the molecular weight range 60 to about 500, more preferably 60 to about 450.

Preferably, the chain extender of formula (1) has a molecular weight of about 500 or less.

The hydrocarbon radical for substituents R₁, R₂, R₃ and R₄ may include alkyl, alkenyl, alkynyl, aryl and heterocyclyl radicals. It will be appreciated that the equivalent radicals may be used for substituents R₅, R₆ and R₇ except that the reference to alkyl, alkenyl and alkynyl should be to alkylene, alkenylene and alkynylene, respectively. In order to avoid repetition, only detailed definitions of alkyl, alkenyl and alkynyl are provided hereinafter.

The term "alkyl" denotes straight chain, branched or mono- or poly-cyclic alkyl, preferably C₁₋₁₂ alkyl or cycloalkyl. Examples of straight chain and branched alkyl include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, amyl, isoamyl, sec-amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, heptyl, 5-methylhexyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, octyl, 6-methylheptyl, 1-methylheptyl, 1,1,3,3-tetramethylbutyl, nonyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-methyloctyl, 1-, 2-, 3-, 4- or 5-ethylheptyl, 1-, 2- or 3-propylhexyl, decyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- and 8-methylnonyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-, 3- or 4-propylheptyl, undecyl 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-methyldecyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-ethylnonyl, 1-, 2-, 3-, 4- or 5-propyloctyl, 1-, 2- or 3-butylheptyl, 1-pentylhexyl, dodecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-methylundecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- or 8-ethyldecyl, 1-, 2-, 3-, 4-, 5- or 6-propylnonyl, 1-, 2-, 3- or 4-butyloctyl, 1,2-pentylheptyl and the like. Examples of cyclic alkyl include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl and the like.

The term "alkenyl" denotes groups formed from straight chain, branched or mono- or poly-cyclic alkenes including ethylenically mono- or poly-

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unsaturated alkyl or cycloalkyl groups as defined above, preferably C₂₋₁₂ alkenyl. Examples of alkenyl include vinyl, allyl, 1-methylvinyl, butenyl, iso-butenyl, 3-methyl-2-butenyl, 1-pentenyl, cyclopentenyl, 1-methyl-cyclopentenyl, 1-hexenyl, 3-hexenyl, cyclohexenyl, 1-heptenyl, 3-heptenyl, 1-octenyl, 5 cyclooctenyl, 1-nonenyl, 2-nonenyl, 3-nonenyl, 1-decenyl, 3-decenyl, 1,3-butadienyl, 1,4-pentadienyl, 1,3-cyclopentadienyl, 1,3-hexadienyl, 1,4-hexadienyl, 1,3-cyclohexadienyl, 1,4-cyclohexadienyl, 1,3-cycloheptadienyl, 1,3,5-cycloheptatrienyl, 1,3,5,7-cycloocta-tetraenyl and the like.

The term "alkynyl" denotes groups formed from straight chain, branched, 10 or mono- or poly-cyclic alkynes. Examples of alkynyl include ethynyl, 1-propynyl, 1- and 2-butynyl, 2-methyl-2-propynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 10-undecynyl, 4-ethyl-1-octyn-3-yl, 7-dodecynyl, 9-dodecynyl, 10-dodecynyl, 3-methyl-1-dodecyn-3-yl, 15 2-tridecynyl, 11-tridecynyl, 3-tetradecynyl, 7-hexadecynyl, 3-octadecynyl and the like.

The term "aryl" denotes single, polynuclear, conjugated and fused residues of aromatic hydrocarbons. Examples of aryl include phenyl, biphenyl, terphenyl, quaterphenyl, phenoxyphenyl, naphthyl, tetrahydronaphthyl, anthracenyl, dihydroanthracenyl, benzanthracenyl, dibenzanthracenyl, 20 phenanthrenyl and the like.

The term "heterocyclyl" denotes mono- or poly-cyclic heterocyclyl groups containing at least one heteroatom selected from nitrogen, sulphur and oxygen. Suitable heterocyclyl groups include N-containing heterocyclic groups, such as, unsaturated 3 to 6 membered heteromonocyclic groups containing 1 to 4 25 nitrogen atoms, for example, pyrrolyl, pyrrolinyl, imidazolyl, pyrazolyl, pyridyl, pyrimidinyl, pyrazinyl, pyridazinyl, triazolyl or tetrazolyl; saturated 3 to 6-membered heteromonocyclic groups containing 1 to 4 nitrogen atoms, such as pyrrolidinyl, imidazolidinyl, piperidino or piperazinyl; unsaturated condensed heterocyclic groups containing 1 to 5 nitrogen atoms, such as, indolyl, 30 isoindolyl, indolizinyl, benzimidazolyl, quinolyl, isoquinolyl, indazolyl, benzotriazolyl or tetrazolopyridazinyl; unsaturated 3 to 6-membered

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heteromonocyclic group containing an oxygen atom, such as, pyranyl or furyl; unsaturated 3 to 6-membered heteromonocyclic group containing 1 to 2 sulphur atoms, such as, thienyl; unsaturated 3 to 6-membered heteromonocyclic group containing 1 to 2 oxygen atoms and 1 to 3 nitrogen atoms, such as, oxazolyl, isoazolyl or oxadiazolyl; saturated 3 to 6-membered heteromonocyclic group containing 1 to 2 oxygen atoms and 1 to 3 nitrogen atoms, such as, morpholinyl; unsaturated condensed heterocyclic group containing 1 to 2 oxygen atoms and 1 to 3 nitrogen atoms, such as, benzoxazolyl or benzoxadiazolyl; unsaturated 3 to 6-membered heteromonocyclic group containing 1 to 2 sulphur atoms and 1 to 3 nitrogen atoms, such as thiazolyl or thiadiazolyl; saturated 3 to 6-membered heteromonocyclic group containing 1 to 2 sulphur atoms and 1 to 3 nitrogen atoms, such as, thiadiazolyl; and unsaturated condensed heterocyclic group containing 1 to 2 sulphur atoms and 1 to 3 nitrogen atoms, such as benzothiazolyl or benzothiadiazolyl.

15 In this specification, "optionally substituted" means that a group may or may not be further substituted with one or more groups selected from oxygen, nitrogen, sulphur, alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, alkynyoxy, aryloxy, carboxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloalkynyoxy, haloaryloxy, 20 nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, azido, amino, alkylamino, alkenylamino, alkynylamino, arylamino, benzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, acyloxy, aldehydo, alkylsulphonyl, arylsulphonyl, alkylsulphonylamino, arylsulphonylamino, alkylsulphonyloxy, arylsulphonyloxy, heterocyclyl, heterocycloxy, 25 heterocyclylamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, arylthio, acylthio and the like.

Suitable divalent linking groups for R₇ include O, S and NR wherein R is hydrogen or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical.

30 Preferred chain extenders of formula (1) are 1,3-bis(4-hydroxybutyl)

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-tetramethyl disiloxane (compound of formula (1) wherein R₁, R₂, R₃ and R₄ are methyl, R₅ and R₆ are butyl and R₇ is O), 1,4-bis(3-hydroxypropyl)tetramethyl disilylethylene (compound of formula (1) wherein R₁, R₂, R₃ and R₄ are methyl, R₅ and R₆ are propyl and R₇ is ethylene) and 1,4-bis(3-hydroxypropyl)tetramethyl disiloxane.

In a preferred embodiment, the chain extender of formula (1) defined above is combined with a chain extender known in the art of polyurethane manufacture.

According to another aspect the present invention provides a non-elastomeric polyurethane composition which includes a chain extender of general formula (1) defined above and a chain extender known in the art of polyurethane manufacture.

The chain extender known in the art of polyurethane manufacture is preferably selected from the group comprising 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, 1,9-nonenediol, 1,10-decanediol, 1,12-dodecanediol, 1,4-cyclohexanedimethanol, 1,4-cyclohexanediols and isomers thereof, hydroxyquinone bis(2-hydroxyethyl) ether, 2-ethyl-1,3-hexanediol, 2-butyl-2-ethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol and mixtures thereof. 1,4-cyclohexanedimethanol and 1,4 butanediol are especially preferred.

The silicon chain extender can be used alone or in a range of combinations with known chain extenders. Higher molar percentages of the conventional chain extenders, particularly cycloalkane diols, lead to polyurethane compositions with improved mechanical properties and heat distortion temperatures. Accordingly, a preferred chain extender combination includes a silicon chain extender of formula (1) and a cycloalkane diol chain extender.

Although the preferred chain extender mixture contains one silicon chain extender of formula (1) conventional chain extender, it is understood that mixtures containing more than two diols may be used in formulations.

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The silicon chain extender can be conveniently prepared by methods reported in the literature³. Further, the compounds such as 1,3-bis(3-hydroxypropyl)tetramethyl disiloxane (BPTD) and 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane (BHTD) are available commercially. A range of such silicon-based chain extenders can also be prepared by using hydrosilylation reaction of the appropriate hydroxy alkene and 1,1,3,3-tetramethyldisiloxane using catalyst such as the Wilkinson's catalyst.

The polyurethane composition of the present invention generally also includes a polyisocyanate.

Thus, the present invention also provides a non-elastomeric polyurethane composition which includes a chain extender of formula (1) defined above and a polyisocyanate.

The polyisocyanates that can be used in the present invention are preferably diisocyanates. The diisocyanates useful in the present invention include aliphatic or aromatic diisocyanates such as:

- 4,4'-diphenylmethane diisocyanate (MDI);
- methylene bis (cyclohexyl) diisocyanate (H_{12} MDI) including the 4,4' isomer, the 2,4'-siomer and mixtures thereof, the geometrical isomers, trans/trans, cis/trans, cis/cis and mixtures thereof;
- p-phenylene diiodocyanate (p-PDI);
- trans-cyclohexane-1,4-diisocyanate (CHDI);
- 1,6-diisocyanatohexane (DICH);
- 1,6-toluene diisocyanate (2,4-TDI);
- para*-tetramethylxylene diisocyanate (*p*-TMXDI) and
- meta*-tetramethylxylene diisocyanate (*m*-TMXDI);
- 2,4- and 2,6-toluene diisocyanate and their isomer mixtures;
- isophorone diisocyanate; and
- 1,5-naphthalene diisocyanate.

It will be appreciated that this list is not exhaustive and that the invention encompasses any polyisocyanates known to be suitable in the manufacture of polyurethanes.

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The polyurethanes of the present invention may be prepared by any suitable known technique familiar to those skilled in the manufacture of polyurethanes. These methods include manual or mechanical mixing with or without any solvents present, casting, reaction extrusion and reaction injection moulding. A preferred method involves mixing the chain extender/or mixture with a polyisocyanate, preferably a diisocyanate, directly. The silicon chain extender is preferably degassed under vacuum at ambient temperature prior to the polymerisation. If desired, a catalyst such as dibutyltin dilaurate at a level of 0.001 to about 0.5wt% based on the total ingredients and any other desirable additives (eg: antioxidants) may be added to the initial mixture. The appropriate amount of diisocyanate is then added to the silicon chain extender and stirred rapidly to form a clear solution, usually about 30 to 90 seconds, and the polymer cured in an oven at temperatures between 40 and 120°C.

When mixtures of chain extenders are used the polymerisation may be carried out, first by preparing the chain extender mixture with the desired proportions and then vacuum degassing, followed by adding to the diisocyanate. Alternatively, the preferred method is to add the silicon chain extender first to the diisocyanate and stirring the mixture until the solution becomes clear, and the second chain extender is added quickly afterwards with stirring.

Thus, the polyurethane composition of the present invention may be further defined as comprising a reaction product of:

- (i) a diisocyanate or a polyisocyanate; and
- (ii) a silicon chain extender or a chain extender mixture defined above.

In another aspect, the present invention provides a method of producing a polyurethane including reacting a polyisocyanate with a silicon chain extender or a mixture of chain extenders including a silicon chain extender.

The amounts of the chain extender or mixture of chain extenders and diisocyanate or polyisocyanate are chosen, so that the number of moles of the chain extender functional groups (for example hydroxyl groups) are equal to the number of moles of the isocyanate functional groups. It is understood in the art of making polyurethanes that a small excess of about 5 mol % of either the

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chain extender or the diisocyanate may be used. When mixtures of two or more chain extenders are used, any combination of chain extender molar ratios could be used provided the total mixture is equimolar with the diisocyanate.

The polyurethanes may be processed by conventional methods such as extrusion, injection and compression moulding without the need of processing waxes. If desired, however, conventional polyurethane additives such as catalysts, antioxidants, stabilisers, lubricants, dyes, pigments, inorganic and/or organic fillers, and reinforcing materials such as impact modifiers can be incorporated into the polyurethane during preparation.

Polyurethanes of the present invention are easily adaptable to a variety of fabrication techniques including solvent casting, blow moulding, machining to various shapes and other conventional processing techniques such as injection moulding and extrusion.

The polyurethane compositions of the present invention are particularly useful in preparing materials having good mechanical properties and clarity, in particular for applications requiring high impact resistance, stiffness, high heat distortion temperature and other structural strength properties similar to polycarbonate, nylon and other engineering thermoplastics. A particularly useful application is in biomaterials, especially for devices and implants requiring one or more of the aforementioned properties.

According to another aspect of this invention there is provided a material having improved mechanical properties, clarity and/or degradation resistance comprising a polyurethane composition which includes a silicon chain extender or a mixture of chain extenders as defined above.

The present invention provides a series of compositions having good mechanical properties, high heat distortion temperature, high flexural modulus, and preferably free of functional groups such as ester, carbonate, and ether making the materials resistant to degradation under oxidative and hydrolytic environments. Further, the polyurethane composition should also show excellent compatibility and stability in biological environments, particularly when implanted *in vivo* for extended periods of time. Most preferably, the

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compositions of the present invention are substantially free of segments derived from polyols having a molecular weight in excess of 500.

Accordingly, the compositions may be used as a biomaterial and the term "biomaterial" is used herein in its broadest sense referring to a material which is used in situations where it comes into contact with the cells and/or bodily fluids of living animals or humans. Thus, the polyurethane compositions in this invention are useful in manufacturing medical devices and implants.

In a further aspect, the present invention provides a medical device, article or implant composed wholly or partly of the polyurethane composition described herein.

The medical devices, articles or implants may include components of cardiac pace makers, cardiac assist devices, heart valves, extra-corporeal devices, blood pumps, balloon pumps, A-V shunts, biosensors, artificial joints, and orthopaedic implants. Because of the inherent high heat distortion temperatures of these materials it is expected that the polyurethanes are particularly useful for devices requiring dimensional stability at temperatures such as the human body temperature.

It is understood that the materials in the present invention will also have applications in the non-medical areas particularly requiring high strength, high flexural modulus, and high heat distortion temperature. Such applications may include their use in the manufacture of structural components for pumps, vehicles, mining screens, laminating compounds, for example in glazing, and etc.

According to yet a further aspect, the present invention provides an article composed wholly or partly of the polyurethane composition described herein.

The following examples will illustrate the scope of the present invention. These examples are not to be considered as limiting the invention in any way.

In the examples, reference will be made to the accompanying drawing in which:

Fig 1 is a DSC thermogram of the polyurethane formed according to US Patent No. 4647643.

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Example 1

Three polyurethanes compositions were prepared using 4,4'-methylenediphenyl diisocyanate (MDI) and three different chain extender combinations. The three combinations were 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane (BHTD) and 1,4-cyclohexanedimethanol (CHDM as a mixture of *cis* and *trans* isomers) in BHTD : CHDM molar ratios of 1:0, 1:1 and 1:3.

BHTD (Silar Laboratories) was degassed at ambient temperature under vacuum (0.1 torr) for 1h prior to polymerisation. CHDM (Aldrich) was melted at 60°C and degassed under vacuum (0.1 torr) for 1h.

All three compositions were prepared by a one-step bulk polymerisation procedure without the use of any catalysts. For the first composition, degassed BHTD (55.68g) was added to molten (50°C) MDI (50.00g) in a polypropylene beaker and stirred rapidly until the solution turns clear. After about 3 min of mixing the viscous polymer was poured onto a teflon-coated tray and curd at 100°C for 6 hours under nitrogen. The cured polymer was a clear and transparent solid. The second composition (BHTD:CHDM = 1:1) was prepared first by adding BHTD (27.821g) into molten MDI (50.00g) and stirring until the solution cleared (about 60 sec stirring) followed by adding CHDM (14.406g). After stirring the mixture for a further 60sec, the viscous polymer was poured onto a teflon-coated pan and cured under similar conditions.

The third composition was prepared by reacting BHTD (13.91g), MDI (50.00g) and CHDM (21.61g) using a procedure similar to that used to prepare the second composition.

All three materials were compression moulded at 200°C to form 1mm thick rectangular plaques which were clear and transparent. Dumbbells punched from this sheet were used to test mechanical properties using an Instron Model 4032 Universal Testing Machine. The thermal transitions of the materials were measured on a Mettler DSC 30 calorimeter in the -150 to 250° temperature range.

Table 1 summarises the molecular weight, mechanical properties and the glass transition temperatures. Figure 1 shows the DSC traces of the three polyurethane compositions. As seen from the results, all three materials exhibited high tensile strength, flexural modulus and Shore hardness. It is 5 noteworthy that the increasing CHDM proportion increases these properties as well as the glass transition temperature.

Table 1. Properties of polyurethane compositions prepared in Example 1

Property	composition-1 (BHTD:CHDM=1:0)	composition-2 (BHTD:CHDM=1:1)	composition-3 (BHTD:CHDM=1:3)
Shore Hardness (D)	75	84	85
Ultimate Tensile Strength (MPa)	60	68	77
Young's Modulus (MPa)	562	713	648
Elongation at Break (%)	20	31	23
Flexural Modulus (MPa)	1795	1940	2130
Molecular Weight (MW distribution)	170000 (1.37)	119600 (1.51)	122000 (1.56)
Glass Transition Temperature- onset mid point, end point (°C)	30 40 58	77 83 88	98 105 112

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Example 2

Example 2 describes the preparation of three polyurethane compositions based on MDI and three different combinations of BHTD and 1,4-Butanediol (BDO). These included BHTD:BDO molar ratios of 40:60, 50:50 and 60:40.

5 The three compositions were prepared by a one-step bulk polymerisation procedure. Both BDO and BHTD were degassed as described in Example 1.

The first composition (BHTD:BDO=40:60) was prepared by weighing degassed BHTD (22.225g) and BDO (10.803g) into a 150mL polypropylene beaker and adding molten (50°C) MDI (50.00g) with rapid stirring. The solution 10 cleared after about 1min, and stirring continued until the mixture starts to increase viscosity. The viscous polymer was then poured onto a teflon-coated pan and cured at 100°C in an oven for 6 hours under nitrogen. A similar procedure was used to make compositions 2 and 3, except that BHTD (27.821g), BDO (9.003g) and MDI (50.00g) were used for composition 2 while BHTD 15 (33.385g), BDO (7.702g) and MDI (50.00g) were used for composition 3.

All three materials were compression moulded to clear and transparent 1mm thick sheets, and dumbbells punched from the sheets were used for testing tensile properties.

Table 2 summarises the GPC molecular weights, tensile properties and 20 thermal transitions measured by DSC. These results demonstrate that the chain extender combination BHTD and BDO also produces materials that are clear and transparent with high flexural modulus, tensile strength and high Shore hardness.

Results further demonstrate that the high proportion of the conventional chain extender (BDO) yields materials with improved mechanical properties and 25 increased glass transition temperature.

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Table 2. Properties of polyurethane compositions prepared in Example 2

Property	compositions-1 (BHTD:BDO=40:60)	composition-2 (BHTD:BDO=50:50)	composition-3 (BHTD:BDO=60:40)
Shore Hardness (D)	80	82	80
Ultimate Tensile Strength (MPa)	62	59	55
Young's Modulus (MPa)	576	629	577
Elongation at Break (%)	10	23	12
Flexural Modulus (MPa)	2140	1960	1675
Molecular Weight (MW distribution)	86160 (1.47)	129990 (1.49)	84700 (1.48)
Glass Transition Temperature - onset, mid point, end point (°C)	67 74 81	53 61 69	55 61 67

Example 3

5 This example illustrates the preparation of three polyurethane compositions based the aliphatic diisocyanate hydrogenated MDI ($H_{12}MDI$ from Aldrich). The first two compositions were based on a mixture of BHTD and CHDM in 1:3 and 1:1 molar ratios, and the third composition was based on BHTD and BDO in 1:1 molar ratio. The diisocyanate was a mixture of three

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isomers, and was used as received. BHTD and CHDM were degassed according to procedures described in example 1 and BDO as in example 2.

The first composition (BHTD:CHDM=1:3) was prepared by reacting BHTD (2.654g), CHDM (4.1226g), dibutyltin dilaurate catalyst (0.001g) and 5 H₁₂MDI (10.00 g). The degassed chain extenders and the catalyst were weighed in to a 25mL polypropylene beaker and the diisocyanate heated to 60° was then added quickly in to the beaker and rapidly stirred for 1 min. The polymer was cured in the beaker by placing in an oven at 100°C for 12 hours under nitrogen.

A similar procedure was used to prepare second and third compositions, 10 except that the second composition (BHTD:CHDM=1:1) was based on;

- (I) 5.308g of BHTD, 2.748g CHDM, 0.001g dibutyltin dilaurate, and 10.00 g H₁₂MDI,

while the third composition (BHTD:BDO = 1:1 was based on;

- (ii) 5.308g of BHTD, 1.717 g BDO, .001g dibutyltin dilaurate, and 15 10.00 g H₁₂MDI.

All three polyurethane compositions were clear, colorless, and transparent. The polyurethanes were compression moulded to 1mm thick plaques at 200°C, and dumbbells punched from the sheets were tested for tensile properties on an Instron tensile testing machine. Tensile properties, DSC results, 20 and molecular weights of the polyurethanes are summarised in Table 3. It is noteworthy that even with the aliphatic diisocyanate materials with glass transition temperature of nearly 100°C could be produced.

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Table 3. Properties of polyurethane compositions prepared in Example 3.

Property	composition-1 (BHTD:CHDM= 25:75)	composition-2 (BHTD:CHDM= 50:50)	composition-3 (BHTD:BDO= 50:50)
Shore Hardness (D)	75	72	73
Ultimate Tensile Strength (MPa)	77	67	60
Young's Modulus (MPa)	653	613	522
Elongation at Break (%)	15	28	31
Flexural Modulus (MPa)	1776	1590	1720
Molecular Weight (MW distribution)	143600 (1.61)	154720 (1.66)	162390 (1.72)
Glass transition Temp. on set, mid point, end point (°C)	94 101 109	65 71 77	76 83 89

Example 4

Example 4 describes the preparation of a polyurethane composition based on MDI and a mixture of BPTD:CHDM in a molar ratio (25:75). BPTD ((1,3-bishydroxypropyl) tetramethyldisiloxane) was a commercial reagent purchased from ShinEtsu Chemical Company Ltd (Japan). The composition was prepared by a one-step bulk polymerisation procedure, and both CHDM and BPTD were degassed as described in Example 1.

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In this example the silicon-based chain extender was added to MDI first followed by the conventional chain extender CHDM. Degassed BPTD (5.005g) was added to molten (50°C) MDI (20g) in a polypropylene beaker and stirred rapidly until the solution turns clear followed by adding CHDM (8.643g). After 5 about 1 min of stirring, the viscous polymer was poured onto a teflon-coated tray and cured at 100°C for 6 hours under nitrogen. The cured polymer was a clear and transparent solid.

The material was compression moulded at 200°C to form a 1mm thick sheet and dumbbells punched from the sheet were used for testing tensile 10 properties. Ultimate tensile strength 68 MPa, Young modulus 419 MPa, elongation at break 23%, 82 Shore D hardness.

Example 5

This example describes the preparation of a polyurethane composition 15 based on MDI and a mixture of 1,4 bis(3-hydroxypropyl) tetramethyldisilyethylene (HTDE) and CHDM the mole ratio of HTDE to CHDM was 25:75.

The composition was also prepared by reacting HTDE (5.245g), MDI (20g) and CHDM (8.643g) using a procedure similar to that described in 20 example 4. The cured polyurethane was compression moulded under similar conditions and tested for its tensile properties. The material showed 67 MPa ultimate tensile strength, 464 MPa Young modulus, 22%, elongation at Break, and 78 Shore D hardness.

25 **Example 6**

This example illustrates the preparation of a polyurethane based on HTDE:CHDM (25:75) and the aliphatic diisocyanate hydrogenated MDI (H₁₂MDI, Aldrich). The polyurethane was prepared by reacting HTDE (2.501g), CHDM(4.122g), H₁₂MDI(10g) and dibutyltin dilaurate (0.001g) and H₁₂MDI 30 (10g). A mixture of the degassed chain extenders and the catalyst were weighed in to a 25mL polypropylene beaker and the diisocyanate heated to 60°C was then

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added immediately into the beaker while stirring simultaneously for 1 min. The polymer was cured in the beaker itself at 100°C for 12 hours under nitrogen.

The polyurethane was compression moulded at 200°C to a 1mm thick plaque and dumbbells punched from the sheet were tested for tensile properties.

5 The material exhibited 70 MPa ultimate tensile strength, 478 MPa Young modulus, 20% elongation at Break and 76 Shore D hardness.

Comparative Example 1

This example demonstrates that the compositions disclosed in the prior art
10 (US Patent No. 4647643) do not provide polyurethanes with high modulus, high heat distortion temperatures or the high mechanical strength that is achievable with compositions disclosed in the present invention.

A polyurethane composition was prepared according to Example 11 of US Patent No. 4647643. The silicon diol (Q4-3667 fluid) used in this example
15 was obtained from Dow Corning Corporation.

The diol Q4-3667 Fluid (7.0g), Terathane T-1000 (53.0g) and BDO (6.667g) were mixed and vacuum stripped (2 torr) at 65°C for a minimum of 30 minutes until the cessation of bubbling was noted. Molten MDI (33.430g) was quickly added to the mixture and stirred rapidly with a stainless spatula. After
20 about 1 minute, the contents were poured into a teflon coated metal tray and heated to 125°C in a nitrogen circulating oven for 1 hour to complete the polymerisation. After cooling to room temperature, the material was granulated and dried at 65°C for 12 hours under vacuum (0.1 torr) before being compression moulded into a flat sheet at temperatures between 190-200°C under
25 a nominal load of 8 tons.

The polyurethane exhibited 11 MPa ultimate tensile strength, 19 MPa Young's modulus, 520% elongation at break and 35D Shore hardness. The heat distortion temperature of the material was -67°C as illustrated in Figure 1. Accordingly, these results clearly demonstrate that US Patent No. 4647643 does
30 not enable the preparation of polyurethane compositions with properties such as

- 20 -

high heat distortion temperature, high modulus and high tensile strength as in the present invention.

References

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2. Z. Wirpsa, Polyurethanes Chemistry, Technology and Applications Ellis Horwood pp118 (1993)
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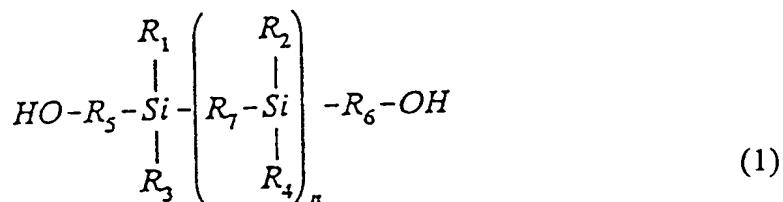
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CLAIMS:

1. A non-elastomeric polyurethane composition which includes a chain extender of the general formula (1)

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wherein

R₁, R₂, R₃, R₄, R₅ and R₆ are the same or different and selected from an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical;

15 R₇ is a divalent linking group or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical; and

n is 0 or greater.

2. A polyurethane composition as claimed in claim 1, wherein the chain extender has a molecular weight of about 500 or less.

3. A polyurethane composition as claimed in claim 1 or claim 2 wherein the hydrocarbon radical is an alkyl, alkenyl, alkynyl, aryl or heterocyclyl radical or an alkylene, alkenylene and alkynylene radical as appropriate.

25 4. A polyurethane composition as claimed in any one of the preceding claims wherein the divalent linking group is O, S or NR wherein R is hydrogen or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical.

5. A polyurethane composition as claimed in any one of the preceding claims wherein the chain extender of general formula (1) is 1,3-bis(4-

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hydroxybutyl)-tetramethyl disiloxane (compound of formula (1) wherein R₁, R₂, R₃ and R₄ are methyl, R₅ and R₆ are butyl and R₇ is O), 1,4-bis(3-hydroxypropyl)tetramethyl disilyethylene (compound of formula (1) wherein R₁, R₂, R₃ and R₄ are methyl, R₅ and R₆ are propyl and R₇ is ethylene) or 1,4-bis(3-hydroxypropyl)tetramethyl disiloxane.

6. A polyurethane composition as claimed in any one of the preceding claims wherein the chain extender of formula (1) is combined with a chain extender known in the art of polyurethane manufacture.

7. A polyurethane composition as claimed in claim 6 wherein the known chain extender is 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, 1,9-nonenediol, 1,10-decanediol, 1,12-dodecanediol, 1,4-cyclohexanedimethanol, 1,4-cyclohexanediols and isomers thereof, hydroxyquinone bix(2-hydroxyethyl)ether, 2-ethyl-1,3-hexanediol, 2-butyl-2-ethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol or mixtures thereof.

15 8. A polyurethane composition as claimed in claim 6 or claim 7 wherein the known chain extender is cyclohexanedimethanol or 1,4 butanediol.

9. A polyurethane composition as claimed in any one of the preceding claims which further includes a polyisocyanate.

10. A polyurethane composition as claimed in claim 9 wherein the polyisocyanate is a diisocyanate.

11. A polyurethane composition as claimed in claim 9 or claim 10 wherein the diisocyanate is an aliphatic or aromatic diisocyanate.

12. A polyurethane composition as claimed in claim 10 or claim 11 wherein the diisocyanate is 4,4'-diphenylmethane diisocyanate (MDI), methylene bis (cyclohexyl) diisocyanate (H₁₂MDI) or isomers thereof, p-phenylene diidocyanate (p-PDI), trans-cyclohexane-1,4-diisocyanate (CHDI), 1,6-diisocyanatohexane (DICH), 1,6-toluene diisocyanate (2,4-TDI), *para*-tetramethylxylene diisocyanate (*p*-TMXDI); *meta*-tetramethylxylene diisocyanate (*m*-TMXDI), 2,4- and 2,6-toluene diisocyanate and their isomer mixtures, isophorone diisocyanate or 1,5-naphthalene diisocyanate.

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13. A non-elastomeric polyurethane composition including a reaction product of:

- (i) a polyisocyanate; and
- (ii) a silicon chain extender or a chain extender mixture as defined in

5 any one of claims 1 to 12.

14. A method of producing a non-elastomeric polyurethane composition including reacting a polyisocyanate with a silicon chain extender or a mixture of chain extenders including a silicon chain extender as defined in any one of claims 1 to 12.

10 15. A material having improved mechanical properties, clarity and/or degradation resistance including a non-elastomeric polyurethane composition which includes a silicon chain extender or a mixture of chain extenders as defined in any one of claims 1 to 12.

16. A material as claimed in claim 15 which is a biomaterial.

15 17. A medical device, article or implant composed wholly or partly of the non-elastomeric polyurethane composition defined in any one of claims 1 to 13.

20 18. A medical device, article or implant as claimed in claim 17 which is a component of cardiac pacemakers, cardiac assist devices, heart valves, extra-corporeal devices, blood pumps, balloon pumps, A-V shunts, biosensors, artificial joints, and orthopaedic implants.

19. An article composed wholly or partly of the non-elastomeric polyurethane composition as defined in any one of claims 1 to 13.

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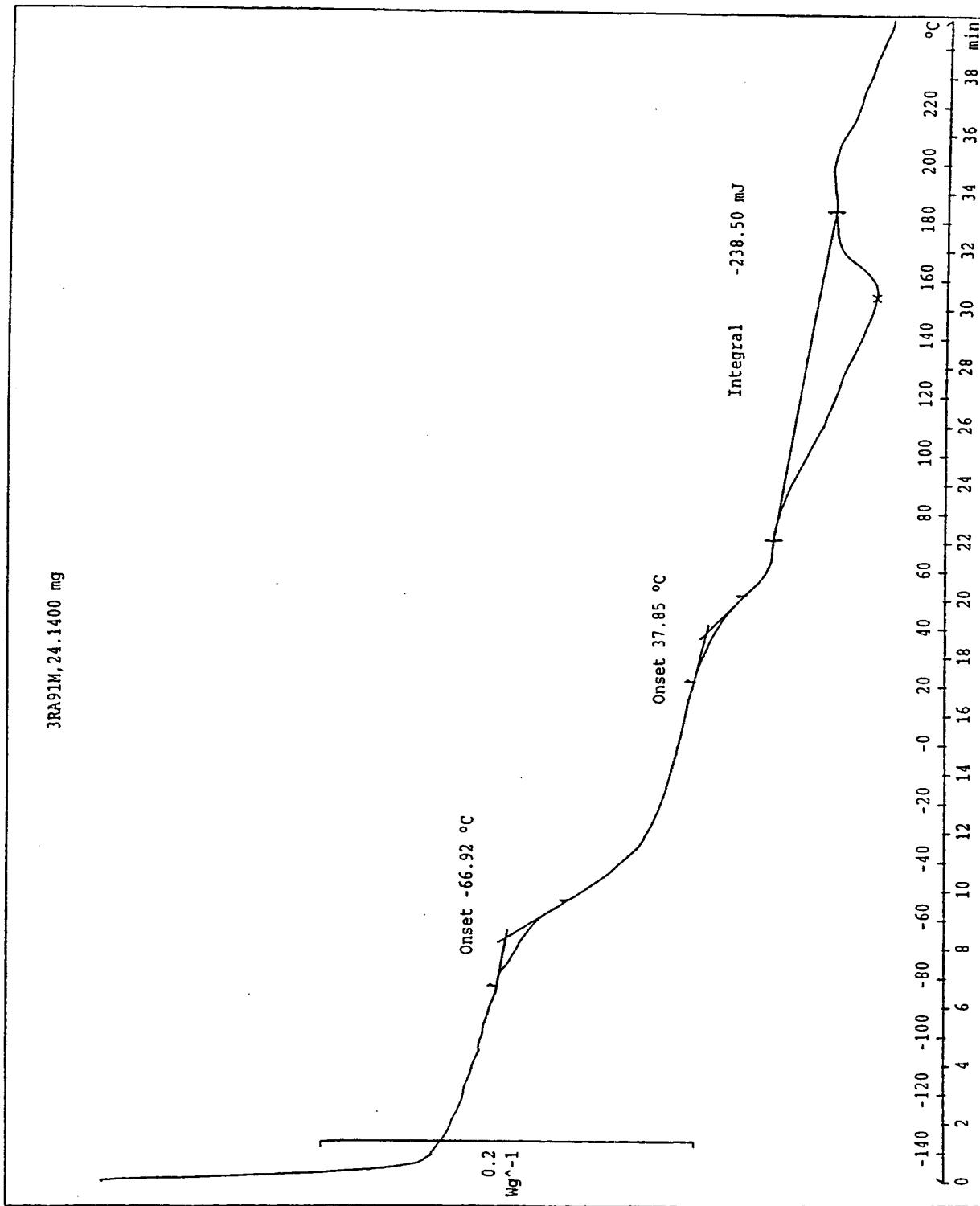


FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 99/00236

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl⁶: C08G 18/32, 18/72, 18/73, 18/74, 18/75, 18/76, 18/61; A61L 27/00, 29/00, 31/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G 18/32, 18/72, 18/73, 18/74, 18/75, 18/76, 18/61; A61L 27/00, 29/00, 31/00; A61F-; A61M-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DERWENT: SILICONE/POLYSILOXANE/SILOCONE DIOL; DIISOCYANATE/POLYISOCYANATE; URETHANE/POLYURETHANE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	AU 41924/97 A (CARDIAC CRC NOMINEES PTY LTD et al), 11 June 1998 page 7, line 1-page 11, line 12; page 13, line 1-page 14, line 21; claims 11-14, 19-36, 41-43	1-19
X	US 5128408 A (TANAKA et al), 7 July 1992 column 13, line 42-column 14, line 36; column 18, lines 3-14; claims	1-4,6-19
X	US 4647643 A (R J ZDRAHALA et al), 3 March 1987 column 2, line 8-column 3, line 25; column 5, lines 49-55; claims	1-4,6-19

Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance		document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed	"&"	

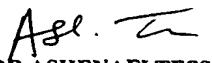
Date of the actual completion of the international search

9 April 1999

Date of mailing of the international search report

21 APR 1999

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 99/00236

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5252683 A (H MURATA et al), 12 October 1993 column 2, lines 28-51; column 4, lines 36-44; column 6, lines 20-43	1-4,6-15
X	US 4758601 A (P HAAS et al), 19 July 1988 column 2, line 15-column 5, line 15; claims 1-3, 5	1-4,6-15
X	EP 230666 A (ESSEX SPECIALITY PRODUCTS), 5 August 1987 page 2, lines 43-49; page 4, line 19; page 5, line 33	1-4,6-15
X	EP 773246 A (BASF AG), 14 May 1997 whole document	1-4,6-15
X	Derwent Abstract Accession No: 92-394001, Class A82, and JP 04292676 (TOYODA GOSEI KK), 16 October 1992 abstract	1-4,6-15
X	Derwent Abstract Accession No: 88-246748, Class A25, and JP 63179916 (DAINIPPON INK CHEM KK), 23 July 1988 abstract	1-4,6-15
X	Derwent Abstract Accession No: 92-264410, Class A25, and JP 04180914 (NIPPON MEKTRON KK), 29 June 1992 abstract	1-4,6-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU 99/00236

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
AU	41924/97	WO	98/13405				
US	5128408	JP	1131226	JP	2115212		
US	4647643	NONE					
US	5252683	DE	4111715	GB	2243369	JP	3292376
US	4758601	BR	8703178	CA	1284699	DE	3621040
		EP	250969	JP	63006025		
EP	230666	AU	67977/87	BR	8700359	CA	1301981
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EP	773246	CA	2189886	DE	19541658	JP	9165431
JP	04-292676	NONE					
JP	63179916	NONE					
JP	04-180914	NONE					
END OF ANNEX							

